scientific highlights

Magnetism

NEUTRONS FOR SCIENCE

Charge order in α-NaV$_2$O$_5$:
complementarity of neutrons and synchrotron radiation

- J.E. LORENZO, S. GRENIER AND Y. JOLY
(LAB. CRISTALLOGRAPHIE, CNRS GRENOBLE)

- B. GRENIER AND L.P. REGNAULT (DRFMC, CEA GRENOBLE)

- O. CEPAS, T. CHATTERJI, A. HIESS AND T. ZIMAN (ILL)

- J.P. BOUCHER (LAB. SPECTROMETRIE PHYSIQUE, UJF GRENOBLE)

The nature of the charge ordering in '-NaV$_2$O$_5$ has fascinated the scientific community during the last years, and the determination of its 3D configuration have challenged both theory and experiments. A variety of experimental techniques have been used, each contributing to a partial but nevertheless incomplete picture of the charge ordering pattern.

In view of this we have attempted a different approach, that is the use of rather unconventional crystallographic methods. As we shall explain below it is the combination of inelastic neutron scattering performed at the ILL triple axis spectrometers IN8 and CRG/CEA-IN22 with resonant X-ray diffraction experiments performed at the ID20 ESRF beamline that has led us to solve this problem.

The problem of charge ordering in '-NaV$_2$O$_5$ has been widely discussed since the early stages of the work. Indeed the room temperature structure was believed to contain 2 different V-sites, with valence states V^{4+} (of electronic configuration $3d^1$ carrying a S=1/2) and V^{5+} ($3d^0$). Recent refinements [1] turn out to consistently converge towards a more symmetric space group with only one V-site assigned as $V^{4.5+}$. Interestingly, this compound undergoes a rather unusual antiferromagnetic order below T_C=34K, characterised by a S=0 non-magnetic ground state separated from the first S=1 excited state by an energy gap: only the excitations carry on the magnetic

The analysis and understanding of the low temperature structure is the goal of this work. On the basis of physical considerations, several theoretical models of charge ordering have been proposed [3], as for instance an alternating order of V^{4+} and V^{5+} in-line chains or a zig-zag arrangement of both species in the rungs of the ladders. Previous X-ray and neutron structural refinements have been hindered by the large size of the unit cell (2a 2b 4c) and therefore by the large number of uncorrelated parameters present in the refinement. From conventional X-ray diffraction experiments (and refinement) different groups [4] have proposed the solution where only half of the ladders

signature of this new state. In addition, a structural distortion develops below T_C resulting in the appearance of superlattice peaks of modulation wavevector q=(1/2, 1/2, 1/4) [2]. These two very peculiar features are present in the canonical Spin-Peierls compound $CuGeO_3$, and have led, in a first place, to consider ' -NaV_2O_5 as the second inorganic compound belonging to the Spin-Peierls family..

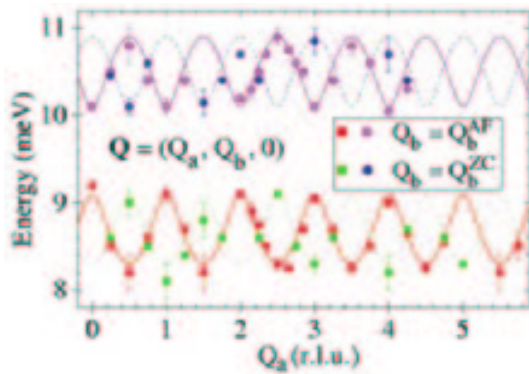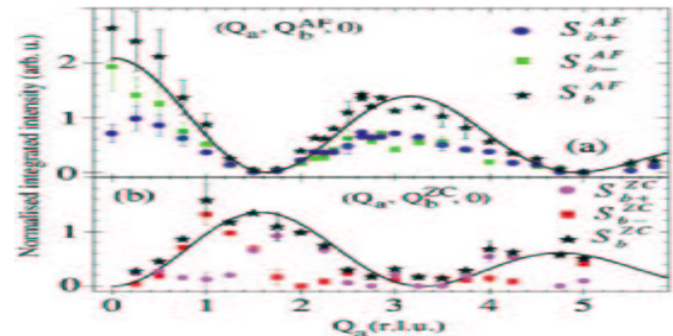

Figure 1: The excitation spectra of ' -NaV_2O_5 is composed of 2 different branches with an energy gap centred at 9.6 meV. Here the dispersion of the two excitations is shown along a*-direction at 2 different Q_b* positions. The structure factor of the upper ones is labelled as $S_{b+}(Q_a)$ and that of the lower ones as $S_{b-}(Q_a)$. The curves are theoretical predictions fitted to the data.

are distorted, which turns out to be in disagreement with, among others, the number of distinct sites found in ^{51}V and ^{23}Na NMR studies [5] and with the number of vibration modes observed in Raman scattering experiments [6].

Another way to access the complex electronic re-distribution occurring below the phase transition is by analysing the structure factor of the magnetic excitations [7]. The magnitude of the dispersion of these excitations reflects the low dimensionality of the magnetic interactions, very dispersive along b* (J_b=60 meV) and nearly dispersionless perpendicular to b* ($J \sim$ 1 meV) (figure 1). Magnetic excitations are supposed to be S=1 triplets, involving two spins in neighbouring rungs, and the spin density in the rung can be directly correlated to electronic density. For simplicity we have purposely misused the V^{4+} and V^{5+} chemical notation to distinguish between both sites in the rung, although each spin is associated with a two-sites electronic wavefunction that depends on the charge density of the rung.

The structure factor of magnetic excitations have been measured along two reciprocal space directions $(Q_{a*}, Q_{b*}, 0)$ with $Q_{b*}=Q^{ZC}_{b*}=1/2$ and $Q_{b*}=Q^{AF}_{b*}=1$ (figure 2). Note that the choice $Q_{c*}=0$ facilitates the calculation as the excitations are projected onto the (a*-b*)-plane,

at the expense of a loss of information on the actual arrangement of the four layers stacked along the c-direction. From this figure one can immediately see that the in-line chain model can be disregarded as, contrary to what has been observed, it should give zero intensity along the $Q_{b*}=1$ line. The experimental data agrees well with the picture where all ladders are modulated in zig-zag, with a fitted charge transfer parameter amounting to 0.3 e (solid lines).
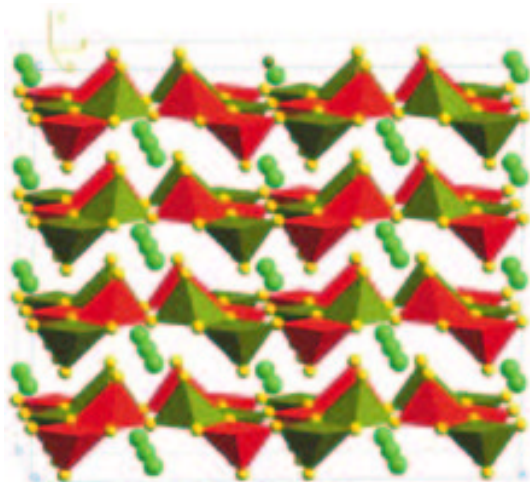

Figure 2: Structure factors (a) $S^{AF}(Q_a)$ and (b) $S^{ZC}(Q_a)$ for the two magnetic branches. Stars represent the sum of structure factors of both branches and the solid line is a fit to a zig-zag model where the correction due the V^{4+}, S=1/2, magnetic form factor has been included.

Figure 3: One of the four possible models of charge ordering of ' -NaV_2O_5 low temperature structure, as obtained from the X-ray resonant scattering experiments [8]. Ladders of pointing-upwards and downwards pyramids alternate along the a-axis and run along the b-direction. Inelastic neutron scattering data shown in figures 1 and 2 [7] have been obtained through a single layer model, corresponding to the first layer from the top. Green(red) pyramids represent large(small) charge densities, $V^{4+}(V^{5+})$ in the chemical notation. Vanadium atoms are located inside the pyramids, closer to their corresponding apical oxygen (in yellow).
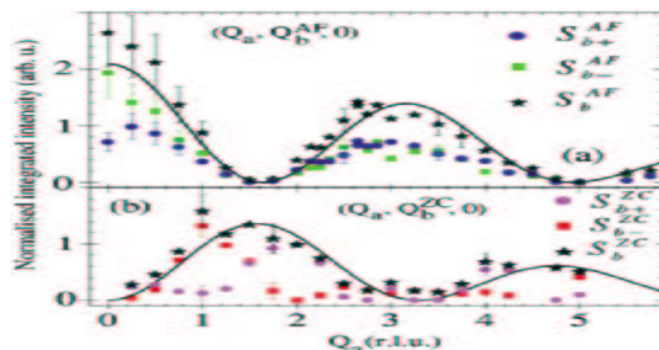
Although the X-ray resonant scattering results [8], not covered here in any detail, are self-contained, the picture issued from inelastic neutron scattering data analysis is fundamental and has served to identify possible solutions and finally to determine the 3D charge order arrangement. The charge ordering pattern deduced from the X-ray results is rather complex, with several degenerated possibilities of stacking of layers along the c-direction (figure 3). Similarly to the neutron data, the deduced charge transferred is rather small (0.1 e) and both results are striking when compared to the bond-valence analysis of the V-O distances that yields a charge transfer of 0.5 e. Finally, and as conclusion, this compound illustrates well how complex the picture of the spin-singlet quantum ground state can be, as well as the manifold of interactions with the underlying lattice.

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